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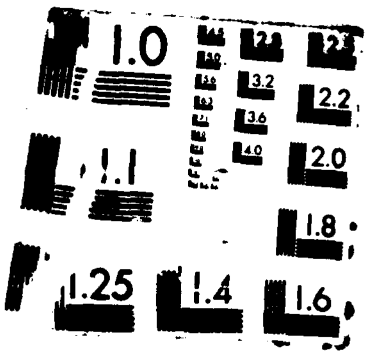
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Report no. : R 86/199
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division of technology for society

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ABSTRACT

Mussels, *Elliptio dilatata*, were collected from a pristine lake and exposed in the Buffalo River, Lake Erie and a confined disposal site, Times Beach, Buffalo, ~~N.Y.~~ New York

The mussels were exposed in a natural way, allowing them to burrow in the sediment or between stones. After a period of about 35 days the mussels were recollected and analyzed for PCBs, DDE and HCB.

The Buffalo River was found to contain bioavailable PCB's and pesticides in three stretches only: 1)

- The two main branches, before they merge into the navigable stretch;
- A stretch passing through several industrial estates downstream of Cazenovia Creek. This stretch is probably affected by an industrial discharge of a mixture comparable to Aroclor 1260; and 3)
- The mouth of the Buffalo River between the Marina and the Coast Guard Station.

In Lake Erie, indications were found for a gradient in PCB concentration.

Mussels exposed in Times Beach, were found to accumulate large amounts of lower chlorinated PCBs and pesticides. Remarkably, they did not accumulate any significant amounts higher chlorinated PCBs (hexa- and heptachlorobiphenyls).

The gamut of PCB congeners in mussels exposed on either side of the endikement enclosing Times Beach revealed no evidence of bioavailable PCBs being transported from Times Beach into Lake Erie.

The present report discusses these findings and makes some recommendations for further research.

1. INTRODUCTION

1.1 GENERAL BACKGROUND

There are several reports and publications on the biomobility of contaminants at "Times Beach", a confined disposal site for dredged materials near Buffalo, N.Y. However, all information collected, so far concentrates on the present situation and processes at the site itself.
Valuable information was collected in 1983 from a series of bioassays with earthworms. These showed that the bioavailability of metals, PCBs and PAHs in the surface layer of the upland position of the site changes with time.

In some cases, there is a growing concern regarding animal uptake, e.g. of cadmium, though for some other contaminants the situation is improving. In 1985 these processes were studied in more detail with the aid of earthworm bioassays, covering a wider range of locations and soil horizons. The analysis of the samples collected is planned for 1986.

The water body of the site was also studied in 1983, when several fish species were analyzed for metals, PCBs and PAHs. Fish were also collected form the very nearby mouth of the Buffalo River as a reference area. The study indicated potential problems in the Buffalo River. Although the concentrations of copper, mercury and arsenic in fish livers from Times Beach and the reference area did not differ very much, cadmium concentrations in fish from the mouth of the Buffalo River were very much higher. Those of PCBs were somewhat lower. The study also revealed that the Corps of Engineers, District of Buffalo, may be faced with the problem of disposing freshly contaminated sedimetn from the Buffalo River. Secondly, the study indicated that the Buffalo River and possible leakage of dikes at Times Beach may affect the quality of life in Lake Erie. In short, the study afforded a first set of data needed for studying the influence of Times Beach on living organisms in its direct surroundings.

A second study worth mentioning in this context is the analysis of young ducks collected at Times Beach. They do not spend their whole lives at Times Beach, but form an inseparable part of the local population that gathers at Times Beach for breeding.

Any detrimental effect of contaminants on the ducks are likely to make themselves felt in a much wider area than Times Beach itself.

1.2 AIMS

The present study is meant to be a first orientation on future problems related to Buffalo River, and on the possible effects of bioavailable contaminants transported from Times Beach into Lake Erie. It is not expected to afford transport models for contaminants, nor to provide answers to all questions it raises. It does, however, point out problems of contaminant uptake, where these occur, and how they might be suitably tackled.

Regarding the bioavailability of PCBs as major pollutant the aims can be stated as follows:

- indicate which stretches of Buffalo River are polluted with them.
- determine their bioavailability in the water body of Times Beach.
- indicate whether Times Beach and Buffalo River are potential sources of bioavailable PCBs in Lake Erie.

1.3 APPROACH

There are several ways of finding how contaminants from Buffalo River and Times Beach get into Lake Erie.
The first is to collect and analyse water samples, data on river discharge, water level fluctuations and rainfall runoff from Times Beach. From these it is possible to estimate the potential input of contaminants into Lake Erie, if it is assumed that the contaminants are not retained by the disposal endikement as a result of adsorption. This approach has the major drawbacks that PCB concentrations in water are difficult to estimate, that it is difficult and time consuming to take account of daily variations, and that far-reaching assumptions have to be made on preconcentration methods and the effects of the dike. A second possible approach is to analyse sediments. This has the drawback that it is difficult to trace sediments to their origin, and to estimate their age. A third approach, the one that is followed in this study, is active biomonitoring. This method utilizes the ability of organisms to concentrate contaminants and integrate daily variations.

This method has the drawback that the concentration of a contaminant in an organism does not necessarily stand in direct relation to its concentration in the water, so that it does not provide a measure of what is being transported. Its salient advantages, however, are that it employs an organism as a self-maintaining concentrator of contaminants of marked uniformity both in behaviour and as an analytical matrix. In addition, the results of the analysis can be directly extrapolated to foodchain relationships. This study being based on active biomonitoring, a short outline of its development is given below.

1.4 BIOLOGICAL MONITORING

Active biological monitoring may look like a novel approach to assess the effects of contaminants on aquatic ecosystems. In fact, it differs in no way from a very ancient one used by miners to detect firedamp with a canary in a cage. An aquatic biological monitoring system also utilizes an organism sensitive to contaminants. Depending upon the scope and aims of the system, the criterion "sensitive" is defined, an a suitable organism is selected. From here onwards, two different approaches can be followed:

- Active biological monitoring makes use of a homogeneous group of organisms collected in the field or raised in the laboratory. This is divided at random into subgroups, and each subgroup is exposed in the field, for instance at different locations. The organisms are called monitor organisms.
- Passive biological monitoring makes use of organisms occurring naturally and collected from different locations. This has the disadvantage that the desired species may not always be numerous enough, or sufficiently uniform in age.

Organisms are called indicators with reference to population dynamic reactions to pollution. Hueck (1976) divides these bioindicators into three classes:

- organisms with negative reaction, which decrease in numbers,
- organisms with neutral reaction, which maintain themselves,
- organisms with positive reaction, which increase in number.

Whether populations of a species decline, maintain themselves or thrive can be inferred from species lists and diversity indices.

Another technique is not to farm organisms out in the field, but as it were to take the field to the organisms in the laboratory. These techniques are generally described as bioassays. Examples have been given for aquatic sediment by Marquenie et al. (1983), and for terrestrial systems by Marquenie and Simmers (1984).

Active biomonitoring with mussels was initially developed for the marine and estuarine environment (Goldberg, 1976, Goldberg et al., 1978, De Kock and Kuiper, 1981). It has been successfully applied in many cases. Its application in the Dutch part of the North Sea and estuaries has been described by De Kock (1983) and De Kock and Marquenie (1981).

Active biomonitoring with fresh water mussels has mainly been developed in the Netherlands by MT-TNO on contract for the Dutch Ministry of Transport and Public Works RIZA (Marquenie, 1981 and 1984). Its development started in 1976, and since its reliability was tested in 1978, it was used on many occasions in the River Rhine (from central Germany downstream) and the River Meuse (from Northern France, through Belgium into the Netherlands). From 1982 onwards it has been routinely employed on a monthly basis at stations where the water quality of the two large rivers that feed Dutch surface water is monitored.

The preferred organism for active biomonitoring is the zebra mussel, *Dreisena polymorpha*, a mytillid species that lives in surface waters attached with byssus threads to solid objects. Another suitable organism has proved to be an unionid mussel, *Anodonta cygnea*, which simultaneously afforded organ specific information on accumulation and elimination rates in field exposures.

Both species are relatively tolerant to pollutants (Marquenie, 1981), and at the same time capable of concentrating contaminants in their tissues. They therefore meet the general demands laid down by Phillips (1977 and 1980) for monitoring organisms.

Results of direct importance to the present study and so far published only in Dutch are summarized below:

- samples composed of the pooled tissues of 60-100 individual *Dreissena polymorpha* or 10-15 individual *Anodonta cygnea* will reduce variability to below an analytical variation of 10%.
- replicate exposures showed that the variability between duplicate samples of pooled individuals falls within the analytical variation of 10%.
- variation in time (season) and place (between locations) can run into orders of magnitude.

This means that, optimally a monitoring network should replicate in time, the inclusive locations which are typical for various microhabitants, rather than replicate for locations at a single time.

- It was found that 40-60 days are needed for equilibrium to be reached in exposed organisms.
- Furthermore the animals should be exposed in the most natural way possible. For this reason *Dreissena polymorpha* is exposed in cages, and *Anodonta cygnea* is stringed and allowed to burrow itself in the sediment.

Concentrations of heavy metals and organic contaminants in the tissues of the animals reflect truly dissolved concentrations in the water, and are not directly related to concentrations of the contaminants in suspended matter or sediment.

An example of such a relation is given for cadmium in Fig. 1, and an example of a concentration gradient of bioavailable cadmium downstream of a point of emission in Fig. 2. The importance of replication in time at a variety of locations is illustrated in Fig. 3.

In the USA and Canada, several species of fresh water mussels have been used. They were selected on basis of experience and local availability. The literature shows that the following genera have also been used for biomonitoring purposes: *Lampsillis spec.*, *Corbicula spec.*, *Elliptio spec.* and *Anodonta spec.*

The present study utilizes the fresh water mussel *Elliptio dilatata*, a mussel occurring naturally in the surroundings of Times Beach and Buffalo River.

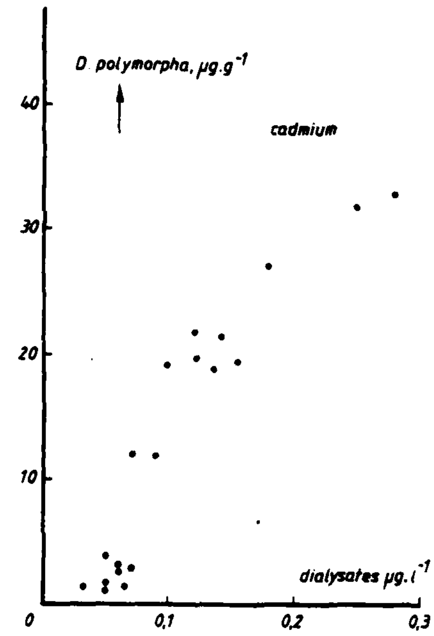

Figure 1. Concentrations of cadmium in *D. polymorpha* (µg/g ash-free dry weight) after 40 days of exposure at various locations in two different rivers compared with concentrations of 'free' cadmium in collected dialysates in situ (µg/l).

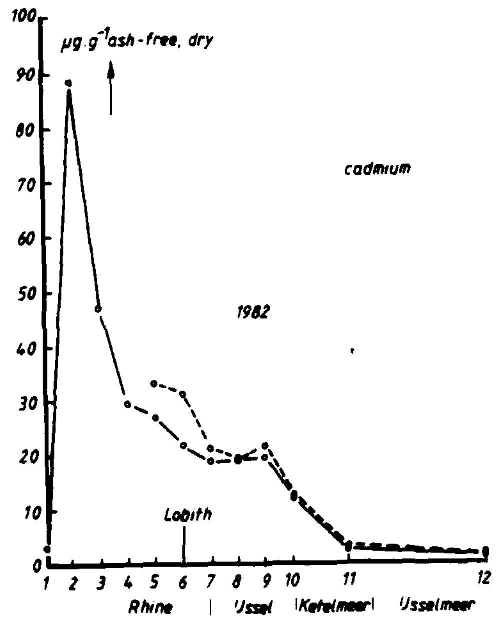

Figure 2. Concentrations of cadmium in soft tissues of *D. polymorpha* (µg/g ash-free dry weight) at various locations in the Rhine and its downstream lakes in 1982. The Rhine enters The Netherlands at Lobith.

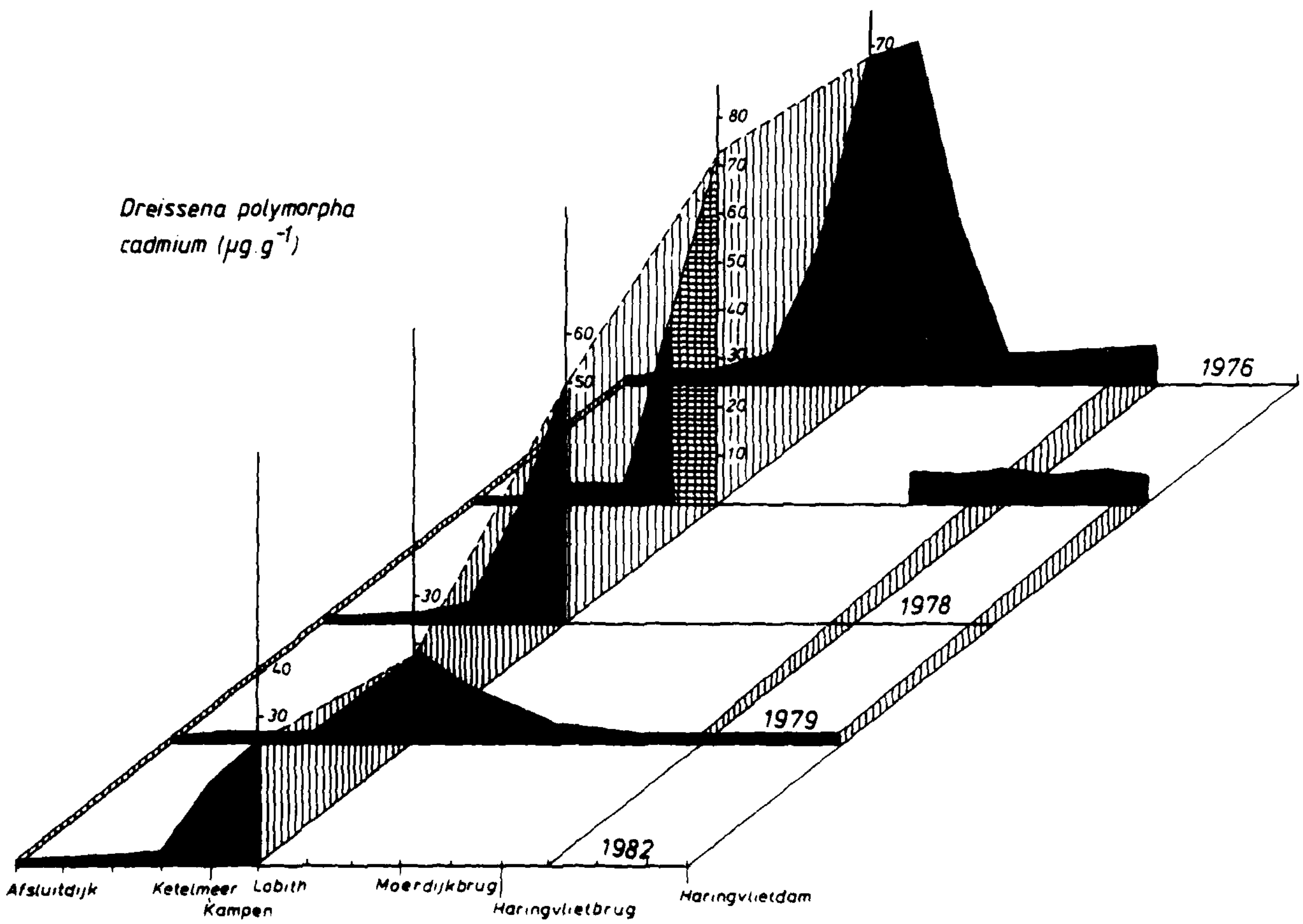

Figure 3. Bioavailability of cadmium in Dutch inland surface waters. Concentrations in *D. polymorpha* (µg/g ash-free dry weight) in successive years (1976-1982) and at different locations. From Lobith, where the Rhine enters The Netherlands, the two main stretches are followed: the river Waal, feeding the Haringvliet basin and the river IJssel, feeding the IJsselmeer.

2. MATERIALS AND METHODS

2.1 SELECTION OF CONTAMINANTS FOR ANALYSIS

Previous results prompted us to restrict the analysis to PCBs. These are regarded as very harmful to the environment. Their concentration and bioavailibility in the water, key parameters for ecotoxicological evaluations, may vary considerably.

2.2 SELECTION OF LOCATIONS

The exposure sites are shown in Figure 4. In the Buffalo River programme the emphasis was on the identification of sources. For this purpose batches of mussels were exposed at more or less regular intervals throughout the river, but particularly at key locations in all stretches adjoining industrial estates and in all branches feeding into the main waterflow.

At Times Beach batches of mussels were exposed in the extensions of transects run into the upland part of the site.

Lake Erie poses the problem that it lacks soft bottom sediments and that the direction of the current in front of Times Beach is uncertain. Locally, the current may be northwards in the direction of Niagara River, following the main flow, but it may be reversed southwards due to overpressure from the Buffalo River and suction from the wave breaker.
We therefore decided to expose the mussels at regular intervals along the dike enclosing Times Beach and at two locations away from Times Beach in a southernly direction. Unfortunately, the wave breaker across from Times Beach, which would have been an excellent reference area, was at the time inaccessible by boat.

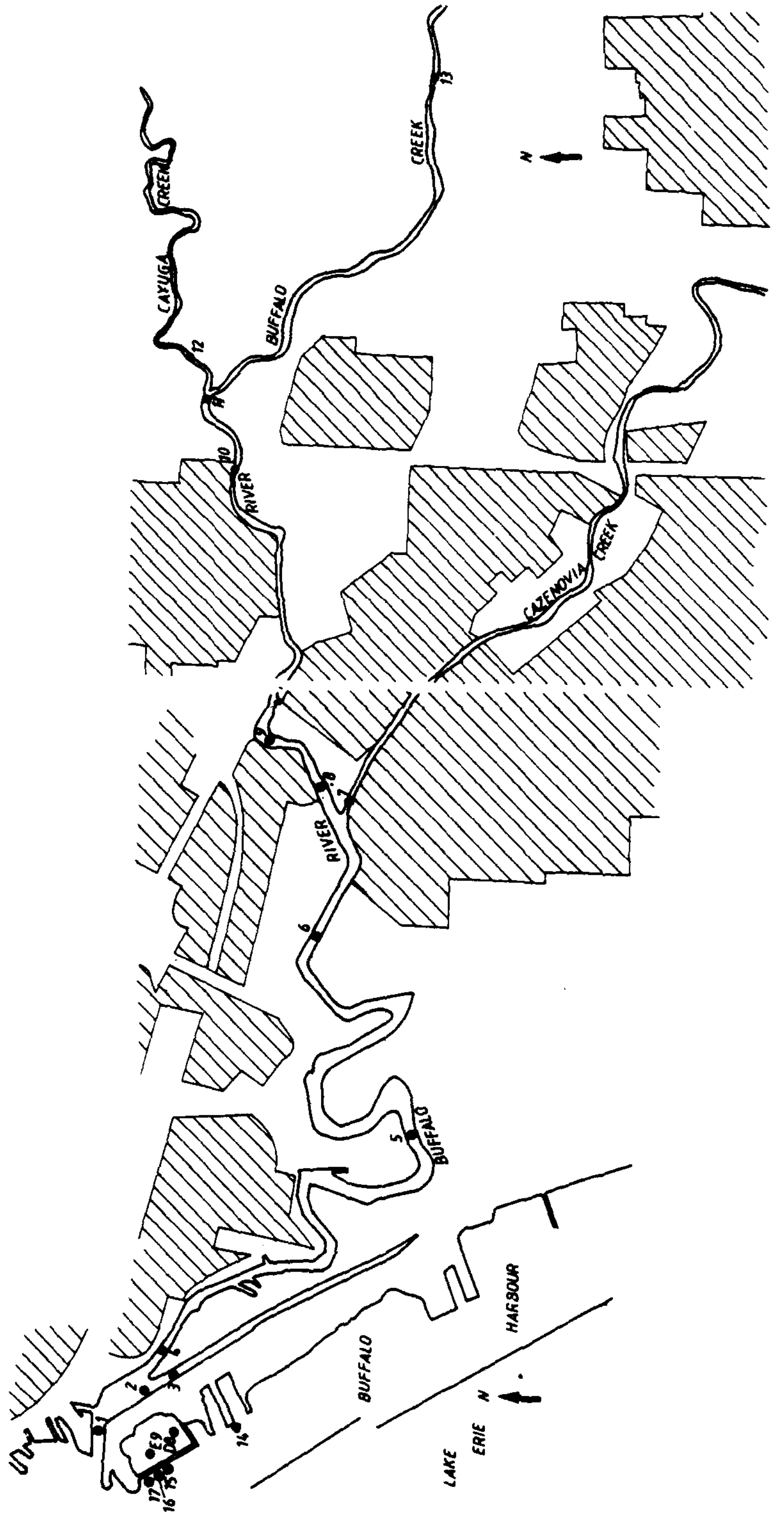

Figure 4. Selection of exposure locations in the Buffalo River, Times Beach and Lake Erie. See also Table 1.

2.3 COLLECTION OF MUSSELS AND PREPARATION OF BATCHES

A suitable location for collecting *Elliptio dilatata*, Chautauqua Lake, was selected in discussions with the Department of Biology, State University of New York at Freedonia, who also supplied divers and a boat to collect the desired number of animals.
These were all collected, sorted according to species and size, and moved to a spot in this lake remote from human activities one week before exposure.
One day before exposure the mussels were recollected, taken to Buffalo and individually glued, with a two-component epoxy, to 50 cm long strings of fine nylon. Each batch consisted of fifteen randomly selected individuals.

The next morning, on May 20, the batches were taken to the exposure sites, and attached to a sufficiently long rope, sunk to the bottom and allowed to burrow in the sediment. The end of the rope was fastened to the nearest available immovable object.

The mussels were recollected 36 days later, were rinsed in the field, stored in polythene bags and frozen on dry ice (-60°Celsius). They were then shipped to TNO laboratories in The Netherlands, and stored at -18°C until needed for analysis.

At the laboratory, the soft tissue of the mussels were dissected with titanium scalpels in acid-washed glassware. The tissues of the mussels from a batch were pooled, their wet weight recorded, and the total sample homogenized with an 'Utra-turrax' equipped with specially made titanium blades. The resulting homogenate serves as a stock, and is stored in a specimen bank. Subsamples are taken for the appropriate chemical analysis, and for determination of dry and ash weight.

The remaining tissue homogenates will be suitably stored for future analysis for heavy metals and organic contaminants. This means that more information can be retrieved without the field programme being rerun.

2.4 ANALYSIS

PCB congeners, op-DEE, pp-DDE and HCB were determined after enzymatic treatment of the homogenate, extraction and clean-up, by means of capillary gas chromatography (CG).

Ash-free dry weight was determined by weighing, drying at 105°C (16 hrs), and ashing at 600°C (24 hrs).

3. RESULTS AND DISCUSSION

3.1 EXPOSURE OF MUSSELS

Table 1 lists the exposure sites and the number of mussels retrieved from each. It also lists the total wet weight of the soft tissues, and the calculated average wet tissue weight per mussel.
Furthermore, it shows that from each batch of 15 mussels, some were lost on all occasions but two, owing to the poor quality of the glue. On some occasions, complete batches of mussels were lost. The batch at the Marina was found wrapped around a piling and could not be lifted, nor could it be retrieved by diving. At the end of the navigable stretch, the main lead was found to be cut. At Lake Erie the leads appeared to be freshly cut on four occasions, and on two further, the rope had been worn away by stones. No mussels were found at these sites, in part owing to the thick layer of algae covering the stones in Lake Erie. Some of the losses may have been due to a heavy storm and to vandalism. For a next occasion it may be better to have the batches put in place and retrieved by scuba divers. The Dutch programmes were also attended by small initial losses, but the experience there gained makes it likely that significant loss can be avoided in future.

Table 2 lists the percentage of ash-free dry tissues and dry tissue. It also lists the calculated average weight of the ash-free dry (organic) tissue per animal.
The table reveals a considerable variation in the percentage of dry tissue and, consequently, in the moisture content of the mussel homogenates. This is due in part to handling, and in part to the internal osmotic status. In order to avoid a bias in the results owing to handling, the analytical results are generally converted to a dry weight basis. An additional bias may result from the salt content of the mussels. This is especially true for mussels living in estuarine environments, because these are ios-osmotic with their surroundings, but also for fresh-water mussels. These contain mainly phosphates and carbonates as salts, whose concentrations vary with the physiological status of the animal. Concentrations of contaminants in this report will be expressed in terms of ash-free dry weight (normalized for organic tissue) in order to avoid bias, and to allow later straight forward calculations of the energy budgets of predators.

TABLE 1 Exposure sites, number of animals retrieved out of 15, total weight per sample (g) and average wet weight per individual (g) Numbers refer to sites on map (Figure 4).

SITE	LOCATION	NUMBER OF ANIMALS	WET WEIGHT WEIGHT (g)	AVERAGE WET WEIGHT (g)
	BUFFALO RIVER			
1	Coast Guard station	8	140.14	17.51
2	Marina	lost		
3	Pilings across from Times Beach	15	225.18	15.01
4	Pilings under skyway	11	215.85	19.62
5	Pilings grain elevator	12	185.34	15.44
6	Across from Allied Chemical	15	317.40	21.16
7	Cazenovia Creek	10	202.78	20.27
8	Bridge upstream from C.Creek	11	206.48	28.77
9	Past Grassy Island	9	143.92	15.99
10	Channel across from bridge	14	170.90	12.20
11	End of navigable stretch	lost		
12	Under bridge of highway	13	232.92	17.91
13	School Rd.	9	139.92	15.54
	LAKE ERIE			
14	Across from Times Beach (1)	2	29.04	14.52
	Across from Times Beach (2)	lost		
	Times Beach -50m	lost		
	Times Beach 50m	lost		
	Times Beach 100m	lost		
	Times Beach 150m	lost		
15	Times Beach 200m	13	173.72	13.36
16	Times Beach 250m	10	164.88	16.48
	Times Beach 350m	lost		
17	Times Beach 400m	4	38.29	9.57
	TIMES BEACH			
	Dike 100m	lost		
	Dike 200m	8	152.80	19.10
	Dike 250m	7	115.80	16.54
	TRANSECT LOCATIONS			
	D6	10	122.54	12.25
	D7	8	118.76	14.84
	D8	12	205.01	17.08
	D8 (float)	2	41.57	20.78
	E6	9	131.76	14.64
	E7	9	159.94	17.77
	E8	9	213.72	23.74
	E9	7	104.57	14.93

TABLE 2. Percentage of ash-free dry material and percentage of dry material in each sample; average ash-free dry weight (g) per individual mussel in each sample.

LOCATION	ASH-FREE DRY WEIGHT (%)	DRY WEIGHT (%)	ASH-FREE DRY WEIGHT, AVERAGE
BUFFALO RIVER			
Coast Guard station	8.59	10.89	1.50
Pilings across Times Beach	8.07	10.85	1.21
Pilings under skyway	9.03	11.64	1.77
Pilings grain elevator	6.68	9.25	1.03
Across from Allied Chemical	7.87	9.79	1.66
Cazenovia Creek	7.70	10.05	1.56
Bridge upstream from C.Creek	9.00	11.43	1.68
Past Grassy Island	6.67	8.90	1.06
Channel across from bridge	5.92	8.25	0.72
Under bridge of highway	5.72	7.71	1.02
School Rd.	4.58	5.77	0.71
LAKE ERIE			
Across from Times Beach	9.73	12.14	1.41
Times Beach 200 m	7.68	9.70	1.02
Times Beach 250 m	5.05	6.85	0.83
Times Beach 450 m	6.52	9.01	0.62
TIMES BEACH			
Dike 200 m	6.54	8.29	1.25
Dike 250 m	9.56	11.55	1.58
TRANSECT LOCATIONS			
D6	5.68	7.77	0.69
D7	6.25	8.08	0.92
D8	6.18	8.41	1.05
D8 (float)	9.55	11.72	1.98
E6	5.01	6.86	0.73
E7	7.07	8.49	1.25
E8	3.83	4.94	0.91
E9	8.10	10.21	1.21

3.2 CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS (PCBs)

Table 3 lists the concentrations of PCB congeners in mussel tissues (ug/kg ash-free dry weight). Some general remarks on the interpretation of the data are in order at this point:

- occasionally, a single peak in a chromatogram is not properly quantified. For this reason the data for PCB-180 at the Buffalo River station (pilings across from Times Beach), and PCB-138 at the Coast Guard should be ignored.

The data show that the Buffalo River is not very heavily contaminated with PCBs. Somewhat higher concentrations were found in the tissues of the mussels exposed upstream, beyond the navigable stretch. Concentrations in mussels exposed in the stretch crossing under the highway were about twice as high as in mussels from the stretches along School Road. In both stretches the current, though shallow, is strong, and the water clear.

Beyond the juncture of the two stretches the river widens, the water deepens and the current loses speed. Here the water becomes turbid from algae and suspended organic matter. These conditions strongly reduce the bioavailability of PCBs to mussels, as is shown by the PCB concentrations found in them at the two locations further downstream. At the bridge, upstream of Cazenovia Creek, PCB concentrations tend to be slightly higher. This may be due to water runoff from the road. Cassanovia Creek itself clearly does not contribute to the pollution of the Buffalo River.

A short increase in PCB concentrations is found in mussels in the river stretch across from Allied Chemical. It indicates that at this point PCBs are discharged into the Buffalo River. The ratio between the different congeners reveals that the discharge is contaminated with a mixture of PCBs in which higher chlorinated compounds predominate. The concominant finding that DDE concentrations at this station were also elevated (see below), leads to two suspected sources:

- surface runoff water or sewage waste water overflow.
- industrial waste water (Aroclor 1260).

Further downstream, the concentrations in the mussels are lower again. This may be due to reduced bioavailability caused by adsorption on suspended matter or sediments.

TABLE 3. Concentrations of PCB congeners in *Elliptio dilatata* (μg/kg ash-free dry weight).

LOCATION	PCB CONGENER (IPUAC) 15	28	52	49	44	70
BUFFALO RIVER						
Mouth of Buffalo River						
Coast Guard station	66.3	45.4	59.3	37,2	89.6	105.9
Buffalo Canal						
Pilings across Times Beach	39.5	3.2	21.7	16.1	-0.8	28.2
Industrial area						
Pilings under skyway	49.6	13.5	34.3	25.2	-0.9	45.1
Pilings grain elevator	40.0	10.6	24.0	18.0	-0.6	30.0
Across from Allied Chemical	63.7	18.8	33.0	42.4	70.8	56.6
Upstream of industrial area						
Cazenovia Creek	36.1	-0.7	5.3	-0.7	-0.7	-0.7
Bridge upstream from Cazenovia Creek	51.3	-0.9	13.5	9.9	-0.9	37.8
Past Grassy Island	40.0	-0.6	-0.6	-0.6	-0.6	-0.6
Channel across from bridge	50.3	-0.5	2.9	-0.5	-0.5	-0.5
Main branches feeding into Buffalo River						
Under bridge of highway	29.7	4.0	7.4	12.5	43.4	13.7
School Road	29.7	2.7	6.4	4.1	33.8	6.4
LAKE ERIE						
Across from Times Beach	73.9	19.4	43.7	12.6	145.9	55.4
Times Beach 200 m	46.8	8.4	21.5	22.2	72.1	23.8
Times Beach 250 m	55.5	2.5	7.0	9.0	42.9	9.0
Times Beach 450 m	51.5	-0.6	5.2	-0.6	-0.6	-0.6
TIMES BEACH						
Endikement						
Dike 200 m	26.8	33.3	91.5	65.4	30.7	91.5
Dike 250 m	61.1	124.2	200.7	143.4	95.6	181.6
TRANSECT D						
D6	52.8	142.0	210.1	153.3	130.6	181.7
D7	31.8	100.0	143.7	106.2	81.2	131.2
D8	42.0	86.5	148.3	111.2	74.1	154.5
D8 (float)	34.3	143.2	276.9	210.1	429.7	286.5
TRANSECT E						
E7	50.9	148,4	219.1	169.6	134.3	212.1
E8	26.0	68.9	111.0	84.2	61.2	118.7
E9	40.5	145.8	251.1	186.3	129.6	259.2

TABLE 3. (Cont.)

LOCATION	101	87	153	138	180
BUFFALO RIVER					
Coast Guard station	60.5	30.2	84.9	1.5	50.0
Pilings across Times Beach	-0.8	-0.8	-0.8	-0.8	656.7
Pilings under skyway	-0.9	9.0	-0.9	-0.9	14.3
Pilings grain elevator	-0.6	6.0	-0.6	-0.6	19.4
Across from Allied Chemical	38.5	12.5	75.5	73.9	92.7
Cazenovia Creek	-0.7	3.8	-0.7	-0.7	2.5
Bridge upstream C. Creek	-0.9	7.2	-0.9	-0.9	39.9
Past Grassy Island	-0.6	3.3	-0.6	-0.6	47.9
Channel across from bridge	-0.5	-0.5	-0.5	-0.5	-1.6
Under bridge of highway	7.4	-0.5	10.2	15.4	19.2
School Rd.	1.8	-0.4	4.5	9.6	13.1
LAKE ERIE					
Across from Times Beach	25.2	-0.9	39.8	54.4	24.6
Times Beach 200 m	5.3	-0.7	21.5	28.4	19.5
Times Beach 250 m	2.0	-0.5	8.5	11.6	17.8
Times Beach 450 m	-0.6	-0.6	-0.6	-0.6	-1.5
TIMES BEACH					
Dike 200 m	22.2	18.3	-0.6	-0.6	-1.5
Dike 250 m	55.4	40.1	-0.9	-0.9	8.3
D6	44.3	32.3	-0.5	-0.5	-1.7
D7	21.2	22.5	-0.6	-0.6	-1.6
D8	48.2	32.7	-0.6	-0.6	11.3
D8 (float)	105.0	62.0	-0.9	-0.9	6.2
E7	59.3	39.5	-0.7	-0.7	4.2
E8	35.6	23.7	-0.3	-0.3	13.0
E9	89.1	51.0	-0.8	-0.8	11.1

Remarkably, and for an unknown reason, the PCB concentrations in the mussels rise again at the mouth of the Buffalo River (Coast Guard station). Possible sources in the vicinity are the Marina and Lake Erie. Shipyards are known sources of copper, tin and PCBs from paints. Unfortunately, the mussels exposed at the Marina were lost.

Mussles exposed in Lake Erie showed elevated concentrations of PCBs generally, but were lacking in PCB-87. Seepage of groundwater from Times Beach can be ruled out as a possible cause, because mussels exposed there did not contain any higher chlorinated PCBs.
The results are comparable to those of a fresh water mussel watch in the river Meuse in Europe to the extent that bioavailability decreases downstream from sources (Marquenie et al. 1985). In the Buffalo River, however, the composition of PCB mixtures reveals no clue to sources (with one exception), whereas in the river Meuse the ratios between PCB congeners allowed identification of specific sources.

In summary, elevated PCB concentrations occurred only in mussels exposed in three stretches of the Buffalo River.
Firstly, the two main stretches, which feed into the navigable stretch are already slightly polluted. The sources are situated further upstream and have not been indentified.
Secondly, the industrial area is moderately polluted, mainly with higher chlorinated PCBs, from industries openly discharging waste water into this area.
Thirdly, elevated concentrations occured at the mouth of the Buffalo River. A contribution from Lake Erie at this point can not be fully ruled out.

To identify the sources and confirm the results, further studies are essential. These can be confined to river stretches found to be polluted with biovailable PCBs.

In future dredging operations, account should be taken of PCB contamination of sediments from river stretches, where uptake of PCBs occured, or stretches just downstream.

Mussels exposed in Lake Erie showed an unexpected variation in PCB concentrations. They were exposed from the corner of Times Beach near the Coast Guard station (Times Beach 450 m), to about 400 m to the south of Times Beach. This is in general direction of Betblehem Steel and the newly built disposal facility.
In this direction, the concentrations of PCBs in the mussels apparently increase strongly. Clearly, contamination of this part of Lake Erie (Buffalo Harbour) is not uniform. The area covered in this research was limited, and the true background concentrations of PCBs in mussels in Lake Erie are not known, so the results may well be due to emissions or to currents of unpolluted water.
Very remarkably, the mussles exposed in Lake Erie were found to contain no PCB-87.

The exposed mussles at Times Beach accumulated high concentrations of PCBs. However, the pattern of PCB congeners clearly differs form that in mussels form the Buffalo River and Lake Erie. Times Beach is polluted mainly with lower chlorinated PCBs and little if any of the more highly chlorinated ones (hexa and hepta). Moreover, PCB-87, not detected in mussels from Lake Erie, occured in all mussels from Times Beach.

These observations show that, although the dike enclosing Times Beach is not watertight, Times Beach does not contribute to PCBs in mussels exposed on the Lake Erie side of the endikement.

The mussels exposed at Times Beach showed some variation in PCB uptake. The question whether this variation is due to local differences in PC concentrations in sediments can only be ansewered after analysis of the sediment samples collected. The highest concentrations were found in a sample of mussels kept floating above sediment at station D8, and the lowest in a sample exposed inside the dike (200 m).

3.3 CONCENTRATIONS OF PESTICIDES (op-DDE, pp-DDE and HCB)

Like PCBs, pesticides are already present far upstream in the Buffalo River, before the two main stretches merge (Table 4). The distribution of HCB strongly resembles that of PCBs. That of DDE differs slightly, because it is found in mussels from all locations downstream of the industrial area. The whole stretch is dominated by disused grain elevators.

TABLE 4. Concentrations of pesticides in *Elliptio dilatata* (ug/kg ash-free dry weight

LOCATION	op-DDE	pp-DDE	HCB
BUFFALO RIVER			
Coast Guard station	16.2	48.8	16.2
Pilings across Times Beach	11.1	28.5	-1.2
Pilings under skyway	12.1	18.8	-1.2
Pilings grain elevator	13.4	14.9	2.9
Across from Allied Chemical	15.2	31.7	20.3
Cazenovia Creek	-1.2	5.1	10.3
Bridge upstream from C.Creek	-1.1	9.9	13.3
Past Grassy Island	-1.4	10.4	-1.4
Channel across from bridge	-1.6	5.0	10.1
Under bridge of highway	8.7	26.2	6.9
School Rd.	6.5	21.8	6.5
LAKE ERIE			
Across from Times Beach	8.2	32.8	8.2
Times Beach 200m	6.5	24.7	10.4
Times Beach 250	5.9	21.7	9.9
Times Beach 450m	-1.5	-1.5	9.2
TIMES BEACH			
Dike 200m	27.5	103.9	36.6
Dike 250m	60.6	57.5	17.7
D6	144.3	133.8	42.2
D7	94.4	78.4	25.6
D8	40.4	106.7	35.5
D8 (float)	36.6	85.8	27.2
E7	33.9	96.1	33.9
E8	120.1	203.6	65.3
E9	25.9	97.5	33.3

Pesticide concentrations in Lake Erie are relatively low. As for PCBs, the concentrations at the corner of Times Beach, near the Coast Guard station, were below detectable limits for DDE.

Remarkably, the gradient found in Lake Erie for PCBs, is not found for pesticides or, at any rate, it is less pronounced.

This difference of distribution between PCBs and pesticides more or less proves that the PCB gradient in Lake Erie is a real one, not due to any intrinsic factors within the mussels.

The exposed mussels from Times Beach showed strongly elevated concentrations, which were subject to relatively large variations. These may be due to erratic contamination of disposed sediments. Similar short-range variations in the concentrations of heavy metals in unionid species were found in The Netherlands. They were found to be related to local variations in water transport and sediment contamination.

When collecting samples of sediment we noticed a certain patchiness in the occurrence of firm sandy spots and musky soft spots. Analysis of the samples of sediment collected may well explain the variation in contamination of the mussels.

3.4 STATISTICAL ANALYSIS

Statistical analysis will be posponed until figures become available for background concentrations in the mussels used in this study and for pollutant concentrations in sediment samples ɪrom Times Beach.

The analysis will be performed on grouped data per area or strethc of river, and per congener or selected groups of congeners.

3.5 ECOTOXICOLOGY

The mussels exposed at Times Beach accumulated high concentrations of PCBs and pesticides.
In food chain studies conducted in The Netherlands, diving ducks were fed mussels from a contaminated basin for three years. As a result, the ducks suffered impairment of breeding succes, and, sometimes, breeding faillure, or mortality of embryos. The suspected causes are PCBs, DDE and mercury. For purposes of comparison, the contaminant concentrations in the (fresh water) food mussels are given in Appendix 2, which shows that concentrations of contaminants in mussels exposed at Times Beach were generally lower than those (Haringvliet) responsible for harmful effects in the ducks.

4. CONCLUSIONS

1. Technical problems were encountered in Lake Erie, especially along disposal endikement. The dike is used by the local people of Buffalo for fishing. Some batches of mussels were swept away by violent currents whipped up by a storm, and some were taken away by vandals. Such loses can be prevented if the mussels are put in place by divers.
   Losses of mussels from the exposed batches did not affect the results. At any rate, they can be prevented in future by the use of a different make of glue.

2. The mussels were exposed in the most natural way possible. Floating batches of mussels, not exposed to sediment, showed abnormally high concentrations of PCBs.

3. The mussel watch was successfull in several aspects:
   - well-defined stretches of the Buffalo River were found to be poluted with PCBs and pesticides.
   - Slight pollution is already formed in the two stretches that merge just upstream of the navigable stretch. The industial section is more severely polluted.
   - The general pattern of contamination indicates a wide range of waste waters, and is superimposed indicates a wide range of highly chlorinated PCBs.
     The mouth of the river is again polluted with a wide range of contaminants.
   - In Lake Erie, PCB concentrations show a gradient from one location to another. The restricted area of shoreline covered in this study, and the fact that the direction of the water current is unknown necessitate further studies in order to delineate variations and sources.
   - The mussels exposed at Times Beach were found to contain high concentrations of lower chlorinated PCBs and pesticides. However, the pattern of PCB congeners differed completely from that in mussels exposed on the outside of the dike in Lake Erie.
     It is therefore highly unlikely that, at the time of these investigations, bioavailable PCBs were being transported from Times Beach into Lake Erie.

4. The concentrations found in mussels exposed at Times Beach were high by any standard, and may be of ecotoxicological significance. The PCB concentrations are slightly lower and of a different pattern from those in mussels from large fresh water basins in The Netherlands.
The results explain certain observations on fish made in 1983.

5. RECOMMENDATIONS

1. For the purpose of establishing the reason for the variability in the data from Times Beach, the sediment samples collected and stored should be analysed.
2. Further studies in the Buffalo River should have two aims:
   - identification of sources,
   - estmation of the transport of contaminants by the Buffalo River into Lake Erie.

4. Further studies at Times Beach should be made of the possible effects of organic contaminants on top predators, like waterfowl and rodents.

6. FINAL REMARKS

It should be remarked, finally, that homogenates of mussel tissues are stored for future analysis.

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2: R 86/199 Musselwatching in the Buffalo River, Times Beach and Lake Erie
3: R 86/220 Preliminary inventory of planktonic and benthic organisms at Times Beach
4: P 85/50 Animal bioassays of black rock harbor sediments - Field verification at an experimental wetland-creation disposal site
5: P 87/007 Morton Arboretum Bioassays.

Concentrations of PCBs and pesticides in the soft tissues of *Elliptio dilatata* (μg)kg wet weight)

LOCATION	15	28	52	49	44	70	101	87	153	138	180	op-DDE	pp-DDE	HCB
BUFFALO RIVER														
Coast Guard station	5.7	3.9	5.1	3.2	7.7	9.1	5.2	2.6	7.3	7.3	4.3	1.4	4.2	1.4
Pilings across Times Beach	4.9	0.4	2.7	2.0	-0.1	3.5	-0.1	-0.1	-0.1	-0.1	53.0	0.9	2.3	-0.1
Pilings under skyway	5.5	1.5	3.8	2.8	-0.1	5.0	-0.1	1.0	-0.1	-0.1	1.3	1.1	1.7	-0.1
Pilings grain elevator	6.0	1.6	3.6	2.7	-0.1	4.5	-0.1	0.9	-0.1	-0.1	1.3	0.9	1.0	0.2
Across from Allied Chemical	8.1	2.4	4.2	5.4	9.0	7.2	4.9	1.6	9.6	9.4	7.3	1.2	2.5	1.6
Cazenovia Creek	4.7	-0.1	0.7	-0.1	-0.1	-0.1	-0.1	0.5	-0.1	-0.1	0.2	-0.1	0.4	0.8
Bridge upstream from C. Creek	5.7	-0.1	1.5	1.1	-0.1	4.2	-0.1	0.8	-0.1	-0.1	3.6	-0.1	0.9	1.2
Past Grassy Land	6.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0.5	-0.1	-0.1	3.2	-0.1	0.7	-0.1
Channel across from bridge	8.5	-0.1	0.5	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0.3	0.6
Under bridge of Highway	5.2	0.7	1.3	2.2	7.6	2.4	1.3	-0.1	1.8	2.7	1.1	0.5	1.5	0.4
School Rd.	6.5	0.6	1.4	0.9	7.4	1.4	0.4	-0.1	1.0	2.1	0.6	0.3	1.0	0.3
LAKE ERIE														
Across from Times Beach	7.6	2.0	4.5	1.3	15.0	5.7	2.6	-0.1	4.1	5.6	2.4	0.8	3.2	0.8
Times Beach 200m	6.1	1.1	2.8	2.9	9.4	3.1	0.7	-0.1	2.8	3.7	1.5	0.5	1.9	0.8
Times Beach 250m	11.0	0.5	1.4	1.8	8.5	1.8	0.4	-0.1	1.7	2.3	0.9	0.3	1.1	0.5
Times Beach 450	7.9	-0.1	0.8	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0.6
TIMES BEACH														
Dike 200 m	4.1	5.1	14.0	10.0	4.7	14.0	3.4	2.8	-0.1	-0.1	-0.1	1.8	6.8	2.4
Dike 250 m	6.4	13.0	21.0	15.0	10.0	19.0	5.8	4.2	-0.1	-0.1	0.8	5.8	5.5	1.7
D6	9.3	25.0	37.0	27.0	23.0	32.0	7.8	5.7	-0.1	-0.1	-0.1	8.2	7.6	2.4
D7	5.1	16.0	27.0	17.0	13.0	21.0	3.4	3.6	-0.1	-0.1	-0.1	5.9	4.9	1.6
D8	6.8	14.0	24.0	18.0	12.0	25.0	7.8	5.3	-0.1	-0.1	0.7	2.5	6.6	2.2
D8 (float)	3.6	15.0	29.0	22.0	45.0	30.0	11.0	6.5	-0.1	-0.1	0.6	3.5	8.2	2.6
E6														
E7	7.2	21.0	31.0	24.0	19.0	30.0	8.4	5.6	-0.1	-0.1	0.3	2.4	6.8	2.4
E8	6.8	18.0	29.0	22.0	16.0	31.0	9.3	6.2	-0.1	-0.1	0.5	4.6	7.8	2.5
E9	5.0	18.0	31.0	23.0	16.0	32.0	11.0	6.3	-0.1	-0.1	0.9	2.1	7.9	2.7

Concentrations of PCBs, pesticides and PAHs in the fresh water bivalve *Dreissena polymorpha*. The mussels were collected from the two fresh water basins Haringvliet (polluted) an Markermeer (reference), and fed to ducks for a period of three years. Concentrations based on ash-free dry weights.

PCBs (μg/kg)	HARINGVLIET		MARKERMEER	
15	1573	1425	173	72
28	219	193	43	20
52	397	347	-1	-1
49	287	257	-1	-1
44	602	488	173	190
70	315	411	-1	22
101	506	499	41	24
87	100	83	19	5
153	575	513	47	30
138	205	180	16	13
Pesticides (μg/kg)				
op-DDE	246	231	-1	-1
pp-DDE	82	231	15	8
HCB	126	114	36	24
PAHs (μg/kg)				
phenatrene	7	58	57	10
anthracene	15	15	4	1
fluoranthene	547	578	161	66
pyrene	534	526	90	-51
3,6-dimethyl-phenathrene	-27	-26	-25	-51
triphenylene	492	436	68	-51
benzo(b)fluorene	-41	-39	-37	-38
benzo(a)anthracene	383	334	28	-13
chrysene	465	411	64	-38
benzo(e)pyrene	260	205	-74	-76
benzo(j)fluoranthene	-68	-64	-62	-63
pyrene	37	33	19	9
benzo(b)fluoranthene	315	282	42	20
benzo(k)fluoranthene	150	141	20	10
benzo(a)pyrene	192	167	14	7
dibenzo(a,j)anthracene	-41	-39	-37	-25
Dibenzo(a,i)pyrene	-27	-26	-25	-25
benzo(g,h,i)perylene	178	154	-62	-63
dibenzo(a,h)anthracene	-96	-90	-87	-89
indeno(1,2,3-c,d)-pyrene	97	86	20	10
3-methylcholanthrene	-7	-6	-6	-6
antranthrene	7	7	-4	-4